First-principles all-electron theory of atomic short-range ordering in metallic alloys: D022-versus L12-like correlations

Duane D. Johnson, Sandia National Laboratories
J. B. Staunton, University of Warwick
F. J. Pinski, University of Cincinnati
First-principles all-electron theory of atomic short-range ordering in metallic alloys: $D_{0_{22}}$ versus $L_{1_2}$-like correlations

D. D. Johnson  
Computational Materials Science Department, MS 9161, Sandia National Laboratories, Livermore, California 94551-0969

J. B. Staunton  
Department of Physics, University of Warwick, Coventry CV7 4AL, United Kingdom

F. J. Pinski  
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221-0011  
(Received 17 January 1994)

We use a “first-principles” concentration-wave approach based on a finite-temperature, electronic density-functional, mean-field, grand potential of the random alloy to investigate the high-temperature atomic short-range order (ASRO) in Ni$_{75}$V$_{25}$ and Pd$_{75}$V$_{25}$ solid solutions. Experimentally, these similar alloys both develop $D_{0_{22}}$-type long-range order at low temperatures but different ASRO at high temperatures. Our calculations describe the measured ASRO well. We compare these results with those found for a hypothetical Co$_{75}$Ti$_{25}$ solid solution. Since this alloy orders directly from the melt into the $L_{1_2}$ phase, it should exhibit strong $L_{1_2}$-like ASRO, as we find in our calculations. We analyze the features in the calculated diffuse intensities in terms of various factors in each alloy’s electronic structure. Because we have assumed that the atoms are fixed to the Bravais lattice, we discuss two additional examples, Al$_{75}$Ti$_{25}$ and Ni$_{50}$Pt$_{50}$, to show the limitations of neglecting atomic displacements. Notably, the Onsager cavity fields have been incorporated into the theory to conserve the diffuse scattering intensity over the Brillouin zone and to provide a better description of the long-ranged, electrostatic screening effects.

I. INTRODUCTION

Experiments on many face-centered-cubic (fcc) metallic alloys reveal that those which develop $L_{1_2}$ (or Cu$_3$Au) atomic order are significantly more ductile than those that form $D_{0_{22}}$ order, presumably due to the lack of slip planes. Consequently, the $L_{1_2}$ alloys are more likely to be suitable in structural applications because of their mechanical properties; examples include ordered alloys comprised roughly of 75% iron, cobalt, or nickel together with 25% vanadium or titanium. It is therefore worthwhile to isolate the electronic causes which underly the formation of either $D_{0_{22}}$ or $L_{1_2}$ ordered phases in this fcc family of alloys. Typically, this idea has been pursued theoretically by studying the heats of formation together with obvious changes in the electronic structure of the zero-temperature ordered compounds which stabilize the appropriate atomic structure. On the experimental side, diffuse x-ray and neutron scattering data have provided information on the tendencies of these alloys to develop $L_{1_2}$ or $D_{0_{22}}$-type atomic short-range order (ASRO) at high temperatures, which is frequently indicative of the low-temperature behavior. When combined with various thermodynamic methods these data can sometimes assess the relative stability of phases, for example, as a function of temperature. (Whether from $T = 0$ K calculations or high-temperature experimental data, such approaches neglect the possibly important effects on energy differences due to changes in the electronic structure as the state of long-range order varies as a function of temperature. This will be of import later.) Here, we attempt a similar approach by calculating and analyzing the (high-temperature) ASRO in terms of the underlying electronic features of the high-temperature disordered alloy which contribute to the diffuse intensity, especially those electronic features which might impact on the low-temperature ground state. Ultimately, an understanding of the electronic mechanisms which distinguish the two sorts of ordering tendencies will impact alloy design.

Over the past few years, progress has been made in describing trends in phase diagrams of alloys from detailed models of their electronic structure. In the compositionally disordered state at high temperatures, the compositional correlations often act as precursors to the type of ordered alloy that forms as the alloy is cooled. The framework of concentration waves is ideal for the purpose of describing these correlations. In a companion paper, we have detailed our theory for the compositional correlations based on the electronic structure of the high-temperature, random state using the self-consistent-field, Korringa-Kohn-Rostoker, electronic-multiple-scattering theory in combination with the coherent potential approximation (SCF-KKR-CPA). A strength of the work is that the statistical mechanics of the compositional fluctuations are dealt with in a mean-field approximation which is consistent with the mean-field description of the electronic structure, calculated with the inhomogeneous CPA. This aspect of our approach is discussed more thoroughly in the companion article. Both aspects are improved by incorporating...
Onsager cavity fields, instead of the usual Weiss-like fields.\textsuperscript{15–17} One major effect of the Onsager approach is to ensure that the diffuse intensity is conserved over the Brillouin zone, atypical of most mean-field theories; hence, with this description, the diagonal part of the fluctuation-dissipation theorem is obeyed. Our theory includes both band-filling effects and charge-rearrangement effects, such as charge transfer, resulting from the so-called double-counting contributions to the energetics.\textsuperscript{14,13} Previous to the work presented in the companion paper, the double-counting contributions had been neglected in calculations of ASRO based on the random alloy (see, e.g., Refs. 14 and 12). As shown here and in the companion paper, these can be substantial and cavity fields are very important in coping with such long-range interactions.

In the next section, we briefly outline the theory for the compositional correlation functions, or atomic short-range order, of alloys and summarize key formal results pertinent to this paper. We then discuss five different alloy systems. First, we show our results for Ni\textsubscript{75}V\textsubscript{25}, Pd\textsubscript{75}V\textsubscript{25}, and Co\textsubscript{75}Ti\textsubscript{25} alloys, in an attempt to isolate those band-filling (electron per atom, c/a) and charge-rearrangement effects which cause the first two alloys to form $D_{0h}^{22}$-ordered phases at low temperatures, while the last system forms an $I\bar{1}2$ phase directly from the melt. We discuss the importance of the temperature dependence of the $D_{0h}^{22}$-$L\bar{1}2$ energy difference in the first two systems, especially due to the state of long-range order, which explains some of the previous discrepancies between this difference obtained from $T=0$ K band-structure calculations and high-temperature measurements. Where possible, we compare our results with diffus neutron or x-ray scattering data. Note that in some sense these alloys are all similar, either being iso-electronic or having the same atomic-number differences, but equivalent phases exhibit substantial differences in stability as a function of temperature.

Second, we calculate the high-temperature ASRO in Al\textsubscript{75}Ti\textsubscript{25} and Ni\textsubscript{50}Pt\textsubscript{50} alloys to assess the severity of constraining the underlying crystal lattice to be fixed and rigid, as is done currently. This neglect of static displacement effects limits the applicability of the current formalism, being more severe than the local-density approximation to density-functional theory (DFT) or the use of the atomic-sphere approximation (ASA) in the KKR-CPA calculations. It is clear, for example, from x-ray-absorption fine-structure (XAFS) studies that this assumption is not valid for all systems,\textsuperscript{18} especially big-atom–small-atom alloys. Finally, we close by drawing some overall conclusions.

II. THE COMPOSITIONAL CORRELATION FUNCTION

As preliminary, we note that any alloy configuration, whether ordered or disordered, can be described in terms of a set of site-occupation variables $\xi_i$ which is 1 (0) if an $\alpha$-type atom does (does not) occupy the $i$th site in the lattice. For a binary $A_\alpha B_\beta$ alloy, the Ising-like symmetry requires only one $\xi_i$ per site, for the site is occupied by either an $A$ or $B$ atom. We will restrict ourselves to binary systems here. The thermodynamic average of $\xi_i$, $\langle \xi_i \rangle$, is then the average concentration (or probability) of an $A$ atom at that site, $c_i$. For a homogeneously disordered alloy $c_i = c$ for all sites. We want to predict the type of site-occupational correlations which develop to break this symmetry of the homogeneously disordered alloy as the alloy is cooled.

At very high temperatures the alloy is (assumed to be) homogeneously disordered. This configuration is taken as our reference state for a linear-response investigation of the atomic pair correlations which develop as the temperature is lowered. The now standard KKR-CPA electronic-structure techniques developed for the completely random alloy are then appropriate for describing the reference state, and give a good description of its electronic structure and energetics.\textsuperscript{19,20} Further advantages are also provided by the use of DFT and the use of the CPA due to the variational nature of the KKR-CPA (Refs. 19,13). For an inhomogeneously disordered state, annotated by $\{c_i\}$ which are uncorrelated, a CPA theory can be formally written down but not numerically evaluated because the system of equations is $N \times N$, where $N$ is $O(10^3)$. However, this mathematical approach allows one to generate formally various correlation functions. As detailed in Ref. 13, we proceed in the following manner. If small, inhomogeneous external potentials $\{\delta v_j\}$ are applied to the homogeneously random state, local variations of the site-occupational probabilities, $|\delta c_i|$, are induced and can be calculated via linear-response theory. As a result, the compositional correlation function, and the growth of correlations with lowering temperatures, can be investigated via the fluctuation-dissipation theorem which connects these responses to the atomic pair-correlation function,

$$\alpha_{ij} = \delta c_i / \delta v_j = \beta \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle$$

where $\beta = 1/(k_B T)$.

It is then straightforward within the mean-field approach to obtain the probability of finding an $A$ atom on a site $i$ as

$$c_i = \frac{\exp[-\beta(\delta v_j + v_j)]}{\exp[-\beta(\delta v_j + v_j)] + 1} \quad (1)$$

This follows from mean-field thermal averaging over the chemical degrees of freedom and then the required use of mean-field configurational averaging over the electronic degrees of freedom, as discussed in the companion article.\textsuperscript{13} The effective chemical field obtained is a single-site function $v_j^{eff} = \delta \Omega^{CPA}(c_i)/\delta c_i$. We take the electronic grand potential as obtained by the inhomogeneous CPA, $\Omega^{CPA}(c_i)$, as the electronic basis of our effective chemical Hamiltonian and this can be formally expressed in terms of spin-density-functional theory.\textsuperscript{21} The effective chemical potential difference $v_j$, which preserves the relative numbers of $A$ and $B$ atoms, has been given site dependence as a formal device for taking variations, and, in fact, reflects the contributions from both the internal and applied external fields. Now $\delta c_i / \delta v_j$, i.e., $\alpha_{ij}$, the chemical correlations, may be obtained in which the electronic structure of the disordered state is treated accu-
rately to describe the ASRO from first principles.

At high temperatures and to lowest order in the applied field which varies from site to site, the change to the probability of finding an $A$ atom on the site $i$ can be written in terms of the changes which are induced on all the other sites, i.e.,

$$
\delta c_i = \beta e (1 - c) \left[ \delta (\delta (\Omega) / \delta c_j) + \delta \nu_j \right]
$$

$$
= \beta e (1 - c) \left[ \sum_j S_{ij}^{(2)} [\delta c_j - \delta c_j (\delta c_i)] + \delta \nu_j \right]
$$

$$
= \beta e (1 - c) \delta \nu_i^{\text{avinty}},
$$

(2)

where

$$
S_{ij}^{(2)} = \frac{\delta^2 \Omega (\epsilon_k)}{\delta c_i \delta c_j} |_{\epsilon_k = c \nu_k}.
$$

(3)

The $\delta c_j (\delta c_i)$ is the change of concentration on a site $j$ due to the change $\delta c_i$ on a site $i$, and is discussed below. With $\delta c_j (\delta c_i) = 0$, the term in square brackets is a (first-principles) chemical analog of the Weiss field of mean-field theories of magnetism. Here $S_{ij}^{(2)}$ must be obtained by complete second-order functional derivation of a mean-field, inhomogeneous grand potential which is evaluated in the random state. It inherently depends on the band-filling (electron-per-atom ratio), Fermi-surface and double-counting (i.e., electrostatics and exchange-correlation) effects, all of which are system-dependent effects. Necessarily, the contributions to $S_{ij}^{(2)}$ from band-energy, electrostatic, and exchange-correlation terms are included to the same order in the fluctuations. It also implicitly contains the electron-hole effects through the Fermi factor.

A self-energy effect is included in most standard mean-field approaches, and leads to inaccurate, or even incorrect, results, especially for long-ranged, electrostatic interactions, as shown by Onsager.\textsuperscript{15} To correct this, $\delta c_j (\delta c_i)$ is made finite and the “Weiss” fields are replaced by “Onsager cavity fields,” as discussed by Brout and Thomas.\textsuperscript{16} The cavity field on a particular site $i$ must be chosen such that the variation $\delta c_i$ on that site no longer includes the effects from the induced change of concentration on that site. A sensible prescription for $\delta c_j (\delta c_i)$ is $\alpha_j (\delta c_i)$, or $\alpha_j (\delta c_i) / [\beta c (1 - c)]$ from Eq. (2) (i.e., $\alpha_j c_i^{(1 - c)}$). Now, with this improvement, the site-diagonal part of the fluctuation-dissipation theorem is automatically guaranteed by this prescription, namely, $\alpha_j c_i^{(1 - c)}$. Therefore, the calculated diffuse scattering intensity, as given below, is conserved over the Brillouin zone, atypical for a mean-field theory.

Within this first-principles Onsager approach there are other electronic effects which also must be considered and which are implicitly buried in $S^{(2)}(q)$ and affect the chemical ordering. We consequently resolve $S^{(2)}(q)$ into various components. For example, electronic charge is also rearranged as a consequence of the induced inhomogeneous concentration distribution. We denote these changes by $\delta \rho_{ai}$. In keeping with the ideas underlying cavity fields, the contributions to the concentration change $\delta c_i$, and also the charge alterations $\delta \rho_{ai}$ which accompany it, must not include effects from changes on other sites which arise from the changes on this same site. As above with $\delta c_j (\delta c_i)$, the components $\delta \rho_{ai}$ to the Onsager reaction field are provided by

$$
\delta \rho_{ai} (\delta c_i) = \sum_k (\delta \rho_{ai} / \delta c_k) c_k c_i^{(1 - c)} \delta c_i .
$$

Furthermore, it is also necessary to allow the CPA effective medium to respond via $\delta c_j (\delta c_i)$ to the changes $\delta c_j$ and $\delta \rho_{ai}$ but with all the reaction-field components subtracted out,\textsuperscript{17} including $\delta \rho_{ai} (\delta c_i)$. Here $\delta c_j (\delta c_i)$ are the inhomogeneous changes to the CPA inverse $t$ matrices.\textsuperscript{13,22} Full details and expressions within the SCF-KKR-CPA framework for the lattice Fourier transforms of all the response quantities are given in our companion article\textsuperscript{23} together with technical information on how to evaluate them.

The end result is that $S^{(2)}(q)$ consists of both band-filling terms considered in previous works (indeed, in this limit, equations equivalent to those shown above have been considered by Nicholson \textit{et al.}\textsuperscript{23}) and also charge-rearrangement effects. In terms of concentration wave vectors, following a lattice Fourier transform, we can write ASRO as

$$
\alpha(q) = \frac{\beta c (1 - c) S^{(2)}(q)}{1 - \beta c (1 - c)} - \Lambda_c ,
$$

(4)

with

$$
\Lambda_c = \frac{1}{\beta c (1 - c)} \int dq S^{(2)}(q) \alpha(q) .
$$

(5)

The site-diagonal part of the fluctuation-dissipation theorem is automatically satisfied on solution of these equations, which can be solved numerically by a Newton-Raphson technique. Also, the spinodal temperature $T_s$ may be found. These are equations analogous to a Gorksi-Bragg-Williams model\textsuperscript{14,1,22} for a binary alloy, but are altered by Onsager fields. $S^{(2)}(q)$ plays the role of the lattice Fourier transform of an atomic interchange energy, but has a first-principles electronic basis. Owing to the electronic basis of the theory and its concentration dependence, the theory is much more robust, which can give rise to much different behavior than found historically for the Gorksi-Bragg-Williams model.\textsuperscript{24} Effectively, the Onsager fields renormalize the effective chemical interactions in order to maintain spectral intensity over the zone. Note that each composition of interest requires a new CPA medium, new sets of potentials, etc., to calculate the ASRO.

III. GUIDE TO INTERPRETING THE CALCULATIONS

We now address the physical content of these equations. If $S^{(2)}(q)$ and hence $\alpha(q)$ peak at $|q| = 0$, then the alloy shows clustering correlations. If, on the other hand, $\alpha(q)$ and $S^{(2)}(q)$ have their largest value at some finite $q$, then ordering correlations are signified, with the wave vector $q$ describing the concentration wave. In
many instances, that ordering wave vector also characterizes the low-temperature ordered phase. The spinodal temperature is defined as the highest temperature at which \( \alpha(q)^{-1} = 0 \) for any \( q \). The Onsager corrections always lower this temperature compared to a Gorsky-Bragg-Williams approximation since the effective interactions are always diminished. The largest effects result when long-range interactions are involved, either from electrostatics, as originally discussed by Onsager, or perhaps lattice distortions, which are inherently long ranged, or indeed Fermi-surface-nesting effects.\(^{12}\)

For later discussion, we express the interchange energy \( S^{(2)}(q) \) in terms of three parts,

\[
S^{(2)}(q) = S_{\text{band}}(q) + S_{\text{cross}}(q) - \left( \frac{\Delta Q}{1 + l_{\text{sc}}^2} \right) C(q),
\]

where \( l_{\text{sc}} \) is an inverse electronic screening length and \( C(q) \) the lattice Fourier transform of the electrostatic interaction \( 1/|\mathbf{R}_i - \mathbf{R}_j| \). Given our particular division of space in the electronic-structure calculation (we use the ASA with equal spheres), a site occupied by a particular atom is not necessarily neutral, and this non-neutrality is one measure of “charge transfer” in our model of the alloy. We define \( \Delta Q \) to be the difference in charges when a site is occupied by an \( A \) atom and when it is then occupied by a \( B \) atom. \( S_{\text{band}}(q) \), as discussed by several authors,\(^{12,4,3,25}\) is derived from the filling of electronic states and harbors the Hume-Rothery electron-per-atom-ratio rule.\(^{28}\) If the dominant part of \( S^{(2)}(q) \) given by this piece, then the ordering tendency in the alloy can be discussed in terms of Pettifor’s metallic bonding.\(^{27}\) In addition, from an analysis based on a \( d \)-band tight-binding model, Ducastelle et al.\(^{4}\) and others have shown what ordering tendencies should be expected in several limiting cases where an alloy can be characterized by off-diagonal disorder (i.e., the constituent metals have similar \( d \)-band widths) and diagonal disorder (i.e., the difference between the site energies is large). The standard lore in alloy theory has been as follows. If the \( d \) band is either nearly filled or nearly empty, then \( S_{\text{band}}(q) \) is maximal at \( |q| = 0 \). If, on the other hand, \( d \) bands are roughly half filled, \( S_{\text{band}}(q) \) peaks at finite \( |q| \) values. This simple lore, however, is inapplicable for alloys with substantial off-diagonal disorder, as recently discussed by Pinski et al.\(^{28}\) for Ni\(_{0.5}\)Pt\(_{0.5}\). Based on \( S_{\text{band}}(q) \) calculations, they found that the filling of hybridized bonding \( d \) states below the Fermi energy is an important electronic mechanism behind the \( L_1 \) ordering tendency of this alloy. We provide an update of this story later on in this paper.

The rest of \( S^{(2)}(q) \) coming from the double-counting contribution to the grand potential [i.e., the last two terms in (6)] can be discussed broadly in terms of charge rearrangement. The third term transparently shows one familiar Coulombic part of this and has been pulled out of \( S^{(2)}(q) \) for the purpose of interpreting our detailed calculations. It is likely to be the dominant contribution in “ionically bonded” alloys, to use Pettifor’s categorization.\(^{27}\) It will be sizable for those alloyed compositions of atoms with rather different electronegativities. This term contains explicitly the measure of charge transfer used here, \( \Delta Q \), and electronic screening, the extent of which determines whether metallic or ionic bonding is predominant in a particular alloy. It follows that this third term describes the electrostatic interaction between these equal and opposite charges as a concentration wave develops. In wave-vector space within the first Brillouin zone, this contribution is largest for those values of \( q \) which are compatible with ordering. This term increases monotonically with \( |q| \) and therefore is largest for \( q = (1, 1, 0) \) in a \( fcc \) system. Of course, this electrostatic interaction is screened through an adjustment of the occupation of the electronic states. If the averaged density of states at the Fermi energy of the disordered alloy, \( \bar{n}(\epsilon_F) \), is large, screening is important with the terms producing \( l_{\text{sc}}^2 \) being substantial. In the accompanying paper, we reported on the competition between band filling and this electrostatic effect in nickel-rich Ni\(_{50}\)Cr\(_{0.5}\).

On partitioning \( \bar{n}(\epsilon_F) \) into the partially averaged densities of states associated with \( A \) and \( B \) sites,

\[
\bar{n}(\epsilon_F) = n_A(\epsilon_F) + (1-c)n_B(\epsilon_F),
\]

it is sometimes the case that one portion is somewhat larger than the other. The difference \( \Delta n(\epsilon_F) = n_A(\epsilon_F) - n_B(\epsilon_F) \) is now sizable and consequently the screening effects are taken up by the reoccupation of electronic states associated with one type of site rather than the other. This aspect couples the band-filling and electrostatic contributions to the interchange energy making \( S_{\text{cross}}(q) \) important as well. We will find all three aspects to be playing a role in sorting out the similarities and differences between the Ni\(_{50}\)V\(_{25}\), Pd\(_{50}\)V\(_{25}\), and Co\(_{25}\)Ti\(_{25}\) alloys.

For those alloys characterized by both small effective charge transfers \( \Delta Q \) and \( n_A(\epsilon_F) \) and \( n_B(\epsilon_F) \), the compositional correlations are dominated by the band-filling term \( S_{\text{band}}(q) \). In the companion paper,\(^{13}\) we showed our results for a Cu\(_{50}\)Pd\(_{50}\) alloy, which fell into this category. One of our examples in this paper, the alloy Ti\(_{75}\)Al\(_{25}\), is also in this class. In systems which also have small effective charge transfers, \( \Delta Q \approx 0 \), but differ in that they possess both a sizable \( \bar{n}(\epsilon_F) \) and \( \Delta n(\epsilon_F) \), it turns out that the charge arrangement is still sensitive to the compositional environment and that there is an important contribution to the interchange energy from the second (or cross) term of Eq. (6). This can be considered loosely as an effect coming from local Fermi-energy adjustments as the number of electronic states available varies with atomic composition. Such an occurrence is evident in our calculations of the ASRO of Pd\(_{50}\)Rh\(_{50}\).\(^{13}\)

With this behind us, we now show results of our theory of compositional correlations, or ASRO, for five additional alloys. We will interpret the results in terms of a small number of simple attributes of the electronic structure of the high-temperature, homogeneously disordered alloy. These attributes are (i) the classification of the density of states as either “split band” or “common band,” (ii) the filling of these states (electron-per-atom ratio, \( e/a \)), (iii) the extent of charge transfer in the alloy and, hence, roughly a measure of the species’ electronegativity difference, and (iv) the magnitudes of \( \bar{n}(\epsilon_F) \) and \( \Delta n(\epsilon_F) \).
IV. DO22 VERSUS L12: CORRELATIONS
IN Ni75V25, Co75Ti25, AND Pd75V25 ALLOYS

In this section we are concerned with isolating the electronic causes underlying the formation of either DO22 or L12 ordered phases in a subset of fcc alloys. We compare our calculations for these alloys with band-structure results, as well as diffuse scattering experiments and thermodynamic models based on the diffuse scattering data.

A number of studies have concentrated on the relative stability of DO22 and L12 zero-temperature structures. In particular, Sinha29 spotted an empirical correlation between structure and the number of valence electrons per atom, e/a. For a large number of A3B alloys, he found that the DO22 atomic arrangement is stable for e/a > 8.65, whereas L12 alloys form when e/a < 8.65. Xu, Oguchi, and Freeman1 carried out first-principles, all-electron, local-density, total-energy calculations in both structures for Ni3V, which has e/a = 8.75. In agreement with experiment and with Sinha’s rule, they found that the DO22 structure was the more stable, and stressed the importance of the second-neighbor d-d electron coupling. Pei et al.2 published results with a comparative study of the total energy of Co3Ti (e/a = 7.75) and Ni3V within the linear muffin-tin orbital method (LMTO) and found that, again in accord with experiment, the former alloy has a stable L12 ordered phase while the latter forms a DO22 structure. These results are not easily understood since these two alloys are similar—in the sense that both cobalt and nickel and titanium and vanadium are nearest neighbors in the periodic table.

Moreover, Pei et al. showed that the electronic densities of states n(e) for both alloys in the same structure are rather similar with only a shift in the position of the Fermi energy εF. Towards the top of the d bands, n(e) has a deep trough for both alloys in the L12 atomic arrangement with a more shallow one in the DO22 phase. When εF is above this valley (for larger values of e/a) a portion of the valence electrons must be accommodated in higher-energy states in the L12 structure as compared to the DO22 one and, consequently, on band-filling grounds, the latter structure is energetically favored. Pei et al.2 also noted that the band-filling contribution accounted for most of the energy difference between the two structures for Co3Ti. However, in Ni3V only a fraction of this energy difference was accounted for by band filling—the remainder was provided by an electrostatic (or Madelung) component.

In light of these results, we report on our calculations of the compositional correlations α(q) in disordered Co3Ti25 and Ni3V25 alloys and provide a complementary description of the origins of the ordering tendencies in these alloys. Although Co3Ti crystallizes from the melt straight into the L12-ordered phase, without a solid solution being formed, we nonetheless expect that our calculated α(q) should peak strongly at q=(1,0,0) to signify L12-type correlations. Since Ni3V25 exhibits a first-order phase transition from the fcc solid solution to a DO22 ordered alloy, α(q) is expected to have contributions at both (1,0,0) and (1,1,0), suggesting the onset of a DO22 phase. Of course, strictly speaking, our results are only directly comparable to high-temperature, diffuse neutron and x-ray scattering experiments, and do not necessarily reflect the type of ordered state that the alloy forms at low temperature. As with all the results in this paper, unless otherwise stated, the full theory described in depth in the accompanying paper13 was implemented to produce the results, i.e., band-filling and charge-rearrangement effects are fully incorporated within the framework of the Onsager cavity fields.

Solal and co-workers30 have performed diffuse neutron scattering experiments on a single crystal of disordered Ni75V25 and on disordered Pd75V25 at high temperatures. This latter system also undergoes a first-order phase transition into a DO22-ordered structure and has the same e/a ratio as the nickel-vanadium system. The scattering data reported by Solal and co-workers30 showed, however, some distinct differences—the intensity maxima appeared predominantly about the (1,0,0) and (1,1,0) wave-vector positions in Ni75V25 but only at the (1,0,0) positions in Pd75V25. [For Ni75V25, only a large intensity ridge is found at (1,0,0) which extends from the (1,1,0) absolute maximum.] This interesting circumstance prompted us to include a study of the compositional correlation function of Pd75V25 in this work. Solal and co-workers30 also suggested that the reason for the difference between the ordering indicated by the ASRO and the observed DO22 low-temperature state was due to entropy effects resulting from the second-nearest-neighbor, effective chemical interactions. In particular, the DO22-L12 energy difference was assumed to favor always DO22 as a function of the state of long-range order but entropy (because of the small energy difference) allowed L12-type fluctuations at high temperature (a situation that a Gorsky-Bragg-Williams model should not reproduce because only point entropy is considered).

We begin by showing details of the SCF-KKR-CPA electronic structure of the homogeneously disordered phase, with the fcc lattice spacing obtained from experimental measurements. Figures 1(a), 1(b), and 1(c) depict the densities of states (DOS) of Co75Ti25, Ni75V25, and Pd75V25, respectively. The three plots have many features in common—all are split band in nature, with the states associated with the late transition metal (TM) being nearly fully occupied and those connected with the early TM partially empty. The main difference between the first two plots is simply the position of the Fermi energy, so that the n(εF) of Co75Ti25 has a larger value than that of Ni75V25, mostly due to states associated with the cobalt sites. The DOS of Pd75V25 shows a larger d-band width than the other two systems and, using the jargon of tight-binding models, the alloy has greater off-diagonal disorder. This is reflected in the difference between the d-band widths in the elemental metals. Consequently, the suggestion of some sort of electronic “size effect” that was made for the pair correlations in disordered Ni50Pd50 by Pinski et al.,28 and elaborated upon in a later subsection of this paper, can also be put forward here but is of less significance. All alloys are characterized by quite siz-
able charge transfer $\Delta Q$. For Co$_{75}$Ti$_{25}$, $\Delta Q = 0.355$, for Ni$_{75}$V$_{25}$, $\Delta Q = 0.309$, and in Pd$_{75}$V$_{25}$ $\Delta Q = 0.139$ (in units of electronic charge), and we expect that this aspect will promote compositional correlations commensurate with concentration waves with wave vectors $(1, \frac{1}{2}, 0)$ as mentioned in the last section.

In all cases, charge is transferred from the early to the late transition-metal component, as expected from the requirement that an $A$ atom occupies the same size volume (atomic sphere) as a $B$ atom on the average in the disordered alloy, a construction which is consistent with the single-site nature of the CPA. We have discussed the ramifications of this aspect of the CPA in the companion article. In particular, if unequal sphere volumes had been assigned to each species to minimize $\Delta Q$, this would require that both an $A$ atom and a $B$ atom in an average compositional environment would be neutral, rather than the individual atoms within each configuration being neutral. In essence, this makes $\langle \Delta Q_i \Delta Q_j \rangle$ just $\langle \Delta Q_i \rangle \langle \Delta Q_j \rangle$. It is not clear what such a configurational average means for an unequal sphere construction in the KKR-CPA; in addition, the fluctuations about $\langle \Delta Q_i \Delta Q_j \rangle$ (or higher-order contributions) in such an approach become important and are similar in magnitude to the original terms.

A. Co$_{75}$Ti$_{25}$

In Fig. 2 we show the compositional correlation function for the disordered alloy Co$_{75}$Ti$_{25}$ evaluated at 3500 K, approximately 200 K above the theoretical (spinodal) temperature at which the system would undergo a (second-order) phase transition into an ordered $L1_2$ phase. This high temperature is consistent with the fact that Co$_{75}$Ti$_{25}$ does not form a random solid solution but forms the ordered structure directly on crystallizing from the melt at about $T = 1500$ K. The maxima at the wave vectors $(1,0,0)$ in $\alpha(q)$ describe the system's strong
response to concentration waves that ultimately set up the \(L_{12}\) superlattice.

For comparison, we also implemented the (older) band-energy-only version of the theory which uses only the band-filling contribution \(S^{\text{band}}(q)\) to the interchange energy \(S^{(2)}(q)\), and

\[
\alpha(q) = \beta c \left(1 - c\right) / \left[1 - \beta c \left(1 - c\right) S^{\text{band}}(q)\right].
\]

We found similar \(L_{12}\)-type correlations, albeit with a spinodal temperature \(T_{sp}\) of about 1800 K, some 1500 K lower than the full theory. A similar effect will presumably also be evident in any band-energy-only theory, e.g., Refs. 32, 14, and 33, regardless of any use of improved statistical methods. Ours is not a theory of melting, and therefore it should be made clear that we should not expect to get \(T_{sp}\) close to \(T_{\text{melt}}\), since the physics is quite different for those two quantities. There is then no reason to place more credence in the band-energy-only theory results over the more complete theory. In any case, the approximate half filling of the split bands provides the standard explanation of this behavior.

Although the charge transfer is large in \(\text{Co}_75\text{Ti}_{25}\), the electrostatic contribution to \(S^{(2)}(q)\) is comparatively small owing to the strong metallic screening that is evident in this alloy, shown by both the average density of states and the difference between the density of states associated with Co and Ti at the Fermi energy being large, i.e., \(\bar{n}(E_F) = 24.4\) states/atom Ry and \(\Delta n(E_F) = 17.3\) states/atom Ry. Upon fitting \(S^{(2)}(q) = \Lambda_c\) to real-space (neighboring shell) parameters via \(S^{(2)}_0 + \sum_{i \in n} S^{(2)}_n \exp(iq \cdot R_i)\) (see discussion in Sec. III of the companion paper\(^3\)), we find \(S^{(2)}_c = -68\) mRy and \(S^{(2)}_0 = -31.4, -0.2, \) and 2 mRy, respectively, with subsequent shell parameters of the order of fractions of mRy. It is possible that explicit local environment effects, neglected in the standard CPA, could lead to even more complete screening, thereby lowering the calculated spinodal temperature. The standard CPA neglects explicit charge correlations due to the local chemical environments, as discussed by Johnson and Pinski in their improvement to the CPA.\(^{20}\) Of course, the overall qualitative details that we have found would be unaffected.

An important point can be extracted about the cavity-field construction from the results obtained when it is omitted. The charge contributions to the interchange energy are now dramatically overestimated and the ordering transition temperature jumps to an unrealistic 7300 K. Along parallel lines to Onsager's original deliberations on the polarization of dielectric materials, we can draw a similar conclusion that consideration of cavity fields for such long-ranged charge effects is crucial. More about this will be discussed in a separate paper.\(^{34}\) In summary, we find that the correlations in a fictitious \(\text{Co}_{75}\text{Ti}_{25}\) solid solution are indicative of a stable \(L_{12}\)-ordered phase that is found experimentally, as well as in total-energy calculations. These correlations are driven, for the most part, from an electronic, band-filling mechanism. Notably, the effects coming from \(\Delta Q\) are predominantly screened out.

**B. \(\text{Ni}_{75}\text{V}_{25}\)**

In Fig. 3(a) we depict the calculated \(\alpha(q)\) for the disordered alloy \(\text{Ni}_{75}\text{V}_{25}\) at a temperature of 700 K, roughly 50 K above the theoretical spinodal ordering temperature. The ordering temperature, smaller than the melting temperature, is consistent with the observation that nickel-vandum forms a series of random solid solutions on crystallizing. There are peaks around the \((1,1,0)\) or \(W\) points with slightly less weight around the \((1,0,0)\) or \(X\) points, indicative of \(DO_{22}\)-type correlations, and reflecting the possible development of a low-temperature \(DO_{22}\)-ordered phase. For perfect \(DO_{22}\) order, both \(X\)- and \(W\)-type wave vectors are required.\(^9\) We find good qualitative agreement with the topology of the \textit{in situ} neutron scattering data from a \(\text{Ni}_{75}\text{V}_{25}\) alloy at 1373 K (50 K above the first-order transition temperature) reported by Solal and co-workers,\(^{30}\) except, as mentioned earlier, that they find only large weight at \((1,0,0)\) not a small peak. Our estimated spinodal \(T_{sp}\) is lower than the actual first-order transition, as it should be, but some 50% lower. Interestingly, thermodynamic calculations using the real-space, chemical interactions deduced from the experimental data find that the calculated \(T_c\) is about 20% low, roughly 1100 K.\(^{35}\)

At 700 K, a real-space fit to the calculated \(S^{(2)}(q)'-\Lambda_c\) is long ranged and yields \(S^{(2)}_c = -36.05\) mRy, and, for shells \(-15, S^{(2)}_{-15} = -10.84, 4.761, 0.183, -1.595, -0.249, -0.004, -0.312, 0.012, 0.282, -0.115, -0.019, 0.014, -0.015, 0.000, \) and \(-0.020\) mRy, respectively. We find that at least 15 near-neighbor shells are needed to reproduce accurately our first-principles plot shown in Fig. 3(a). This long-range behavior is also found from the experimental data using an inverse
Monte-Carlo method or cluster-variational method calculation.\(^3\) (For comparison to their Ising-model-like results, \(S^{(2)} = -4J\) for all shells.) Their best fit to experimental ASRO is found with longer-ranged interactions. They only included neighbors out to the ninth shell in their fits, excluding shells 5 and 6. Their first four interactions from this fit are \(-10.64\), \(2.29\), \(0.15\), and \(-1.03\) mRy, respectively. Compared to our calculation, the obvious difference is a smaller second-neighbor interaction. In Ref. 30 \(\alpha(q)\) for Ni\(_3\)V has been measured for a range of temperatures. The second-neighbor interaction is very sensitive to temperature, becoming much larger near the critical temperature. The larger second-neighbor interaction results in a sharper structure around the extremal points for \(\alpha(q)\) and in a larger \(T_c\). We note that displacement effects could also alter the second-neighbor interaction since it is the closest neighbor along the soft direction in a fcc lattice.

Importantly, we also find that the relative intensities at the \(X\) and \(W\) points depend on \(e/a\) and on the temperature. Above 900 K in the Ni\(_{75}\)V\(_{25}\) \((e/a = 8.75)\) calculation, the intensity at the \(X\) point is the largest, whereas between 650 and 850 K the maximum of \(\alpha(q)\) is at the \(W\) point. This suggests that at some higher temperature in the experiment an equivalent switch could be observed. We also checked how the results of the full theory depend on \(e/a\) by varying the concentration of nickel. Our calculated \(\alpha(q)\) for Ni\(_{70}\)V\(_{30}\) \((e/a = 9)\) has pronounced peaks at \(W\) between 830 K (the estimated spinodal temperature) and 1800 K, indicating rather strong D\(_{022}\) tendency. The intensity at the \(X\) point does not correspond to a maximum, but to a saddle point (as found experimentally for 75\% Ni). Above 1800 K, the global maximum in our calculation is at \(X\). For Ni\(_{67}\)V\(_{33}\) \((e/a = 8.35)\), we find that \(\alpha(q)\) has peaks around the \(X\) points for all temperatures. However, for Ni\(_{67}\)V\(_{33}\), we note that Solal and co-workers do not find a peak at the \(X\) point at \(T = 1230\) K.\(^3\) This suggests that this subtle concentration (or \(e/a\)) dependence may be slightly incorrect, due (1) to use of the mean-field CPA, (2) to the neglect of displacements, or (3) to an effect associated with the screening of charges from local environmental effects. \(^20\) Nonetheless, as discussed below, many of our results are qualitatively confirmed by experiment and other independent theoretical approaches.

These results indicate that in nickel-rich Ni\(_{75}\)V\(_{25}\) alloys with concentrations around \(c = 0.75\) the energy difference between D\(_{022}\) and L\(_12\) ASRO diminishes (and changes sign) with decreasing \(e/a\), with the more Ni-rich alloys giving D\(_{022}\)-like fluctuations. Indeed, the energy differences calculated from

\[
S^{(2)}[q=(1,\frac{1}{2},0)] - S^{(2)}[q=(1,0,0)]
\]

are 11.01 mRy for Ni\(_{70}\)V\(_{30}\) at \(T = 850\) K, 0.23 mRy for Ni\(_{75}\)V\(_{25}\) at \(T = 700\) K, and \(-18.27\) mRy for Ni\(_{67}\)V\(_{33}\). These numbers, which are proportional to the D\(_{022}\)-L\(_12\) energy difference, show that the crossover from D\(_{022}\) to L\(_12\) lies between 75\% and 67\% Ni. In terms of the real-space effective interactions, the energy difference \(\Delta E_{022-L12}\) between the perfectly ordered structures is

\[
\frac{1}{2}S_2^{(2)} - S_3^{(2)} + S_4^{(2)} + S_6^{(2)} - 2S_7^{(2)},
\]

including out to nine neighbor shells (or an entire fcc cube). This relationship is true only if the interactions are independent of temperature, which they are not. For Ni\(_3\)V, an estimate of \(\Delta E_{022-L12}\) from the four real-space interactions gives 0.59 mRy in favor of D\(_{022}\), while the nine-shell fit gives 0.03 mRy in favor of L\(_12\), as compared to the experimentally deduced values of 0.61 and 0.91
mRy, both favoring $D_{022}$.\textsuperscript{35} It is the small peak that we find at $X$, but not found in experiment, that makes the $\Delta E_{D_{022}-L_1}$ smaller when including more shells.

This trend, however, is in complete agreement with Sinha's rule in which alloys with $e/a > 8.65$ should exhibit $D_{022}$ ordering. Of course, the calculated $T_{sp}$ variation with $e/a$ also reflects this. That is, Ni$_{57}$V$_{33}$ exhibits $X$-point maxima and $T_{sp} = 1400$ K, Ni$_{59}$V$_{25}$ shows slight $W$-point maxima with $a(q)$ also substantial at the $X$ point and $T_{sp} = 650$ K, and Ni$_{59}$V$_{20}$ shows stronger $W$-point maxima with $T_{sp} = 830$ K. We propose that this calculated concentration and subtle temperature dependence of the compositional correlations in disordered nickel-rich, nickel-vanadium alloys be examined by further neutron scattering experiments on single crystals.

Some evidence for this dependence on $e/a$ and temperature has been recently presented by Finel et al.\textsuperscript{35} They have commented on $\Delta E_{D_{022}-L_1}$ coming from $T=0$ K band-theory calculations, such as those by Pei et al.,\textsuperscript{2} yield about 7.5 mRy in favor of $D_{022}$, while those coming from the effective chemical interactions deduced from experiment are 0.6–0.9 mRy, a factor of 10 smaller. Our results are in rough agreement with the latter results. Finel et al.\textsuperscript{35} have argued that their numbers are more believable than the $T=0$ K band-theory results because, from the same set of interactions, they also nearly reproduce the temperature dependence of the excess energies of conservative antiphase boundaries in the (100) and (111) planes, as measured by Francois.\textsuperscript{35,36} They also argue that this may be a subtle effect not properly dealt with by LDFT. In the same paper, the authors indicate that Pasturel had communicated that the band-theory results for $\Delta E_{D_{022}-L_1}$ are extremely sensitive to $e/a$, using a rigid-band approach to estimate the effect. Since we are using KKR-ASA theory for the electronic structure, it should be clear that the $\Delta E_{D_{022}-L_1}$ that we would calculate would agree with Pei et al. and Pasturel. So, as remarked above, we expect that this energy difference is sensitive to the degree of long-range order present in the calculation, since we have also reproduced the small difference at high temperatures. Obviously, such an effect is particularly important when $E_F$ is in a peak in the $T=0$ K electronic structure for one structure and not for the other, as is the case for Ni-rich Ni-V alloys.

We have also investigated the effects of various approximations on the ASRO. While in many cases we, and other researchers, have found that the band-energy contributions give the basic physics underlying the ordering, as in the Co-Ti alloy above, this is not always the case, as discussed in the companion paper.\textsuperscript{13} If we neglect charge-rearrangement effects and including only the band term $S_{\text{band}}(q)$ in $S^2(q)$, the intensity about the $W$ point for the Ni$_{57}$V$_{25}$ alloy is drastically diminished. In fact, for the three Ni-V alloys mentioned here, including only band-filling terms results in maxima around the $X$ point at all temperatures; no $D_{022}$-like correlations are found, as is shown in Fig. 3(b). There will be similar consequences for any methodology in which only the band-energy terms are considered (independent of any improvement in treatment of the statistical mechanics). This encompasses previous concentration-wave calculations.

As with Co$_{75}$Ti$_{25}$, we also repeated the calculation in which all band-filling and charge effects were included but a standard mean-field theory was implemented rather than the cavity-field formalism. Once again the difference between the results from the two approaches was dramatic. The mean-field version of $a(q)$ has roughly equal peaks around the $X$ and $W$ points but the effective ordering temperature of 5500 K is very high, even above the melting temperature. Unless the long-ranged charge effects are handled within a cavity-field description, they will be overestimated.

C. Pd$_{75}$V$_{25}$

In Fig. 4 we show our theoretical short-range order (scattering intensity) in the (001) plane for Pd$_{75}$V$_{25}$ at 850 K. Topologically, this compares rather well with the high-temperature diffuse neutron scattering measurements of Solal and co-workers\textsuperscript{30} on this system. Both show pronounced maxima at wave vectors $(1,0,0)$ with subsidiary shoulders at roughly $\frac{1}{3}$ of the way along the $(1,1,0)$ directions. The smaller charge transfer in this alloy, in comparison with Ni$_{57}$V$_{25}$, is the cause of the reduced weight around $(1,\frac{1}{3},0)$.

Our calculated real-space parameters at $T=850$ K (200 K above our calculated spinodal temperature) for the first ten shells, i.e., $S^{(1)}_{-1,0}$ are $-13.01, 1.28, -1.90, -2.11, -0.33, 0.12, -0.39, -0.11, 0.54$, and $-0.01$ mRy, respectively, and $S^{(2)}_0$ is $-29.35$ mRy. All subse-

![Fig. 4. In units of $\rho_{\text{e}}(1-c)$, the calculated $a(q)$ of Pd$_{75}$V$_{25}$ at 850 K, 200 K above the estimated spinodal temperature. The $q_x=0$ plane is shown, with contours every 1.0 dimensionless units.](image-url)
quint shell parameters remain on the order of hundredths of mRy up to the twentieth shell. From Ref. 30, the similar parameters determined from experimental data at about 50 K above $T_\alpha$ are $-13.23, 0.41, -1.68,$ and $-1.94$ mRy. We find better agreement in the case where the electrostatic interactions are effectively screened, except for the second-neighbor interaction (which is again a factor of 2–3 larger than that deduced from experiment). While our theory of short-range order correctly finds the maximum in the short-range order intensity at the $X$ point, we are unable to determine why Pd$_{17}$V$_{25}$ undergoes a first-order phase transition to a $D0_{22}$ phase, as this issue lies strictly beyond the scope of this work. However, some important comments are in order. From these high-temperature (calculated) interactions, the estimated $\Delta E_{D0_{22}-L1_2}$ is very small: 0.11 mRy up to fourth neighbors favoring $L1_2$, whereas the few parameters deduced from experiment favor $D0_{22}$ by 0.16 mRy, basically due to the smaller contribution from the second shell in our calculation. This indicates the sensitivity of the estimated $\Delta E_{D0_{22}-L1_2}$ to real-space inversion, both in experiment and theory, especially when the energy difference is small. At high temperatures, then, this energy difference is indeed small, but is found to favor (however slightly) $L1_2$ fluctuations as observed, when all shells are included in the calculation.

Solal and co-workers$^{30}$ have shown (considering only two neighbor interactions) at these high-temperature $L1_2$ fluctuations can arise from cluster entropy effects even if the $\Delta E_{D0_{22}-L1_2}$ is chosen to favor $D0_{22}$ (but only in a small range of parameters, i.e., $S^{(2)}_S$ is the same sign and much smaller than $S^{(1)}_S$). Also, as up to the fourth neighbor was deemed relevant in the inversion of the Pd$_3$V data, they suggested that an effective interaction involving the antiphase energy should play the role of the second-neighbor interaction; i.e., the 0.16 mRy which slightly favors $D0_{22}$ when four shells only are considered from the experimentally deduced parameters. So, with either experimentally determined or calculated interactions, the free-energy difference may be determined by the entropy contributions. However, our good agreement with the experimentally measured topology of ASRO, the “interactions,” and the mean-field basis of our calculation appear to contradict their explanation of the origin of the first-order phase transition, and there is no breakdown of mean-field theory. We have only included the point entropy with this mean-field theory, disregarding entropy from clusters, such as the tetrahedron-octahedron cluster considered for Pd-V.$^{30}$

It would seem that a similar scenario exists to that present in the Ni-V alloys. Namely, $\Delta E_{D0_{22}-L1_2}$ is affected at the phase transition by temperature-dependent changes in the electronic structure, due to the degree of long-range order, to electron-hole effects, and to possible associated volume and symmetry effects up transforming from the disordered to the partially ordered state. All of these effects are different in general for $D0_{22}$ and $L1_2$ structures. For Ni-V, $\Delta E_{D0_{22}-L1_2}$ favors $D0_{22}$ more strongly for decreasing temperature and, at fixed temperature, diminishes for decreasing $e/a$; whereas for Pd-V it changes sign for decreasing temperature. Such effects have heretofore been neglected in interpreting and comparing interactions and energetics derived from high and low temperatures.

In closing, we make some brief remarks about the care one needs when using our calculated interactions. In principle, accurate thermodynamical models, such as Monte Carlo simulations, might be contemplated with the effective pairwise interactions deduced from the calculated $S^{(2)}(q)$. Three cautionary remarks concerning this approach are in order. First, our first-principles calculations of the interchange energy $S^{(2)}(q)$ [extracted from our theory for the compositional correlation function, $\alpha(q)$] originate from a treatment of the compositional correlations in which the electronic and compositional degrees of freedom are handled within consistent levels of approximation. Using these interactions in a theory for improving the description of the entropy is, in principle, inconsistent, since (at minimum) it neglects the effects of the short-range order on the interchange energies. Secondly, if $S^{(2)}(q)$ is rather long ranged when fitted to real-space parameters (as found here owing to the charge-rearrangement effects), it becomes increasingly more difficult to be included in such methods. Finally, if $S^{(2)}_S$ has significant temperature or $e/a$ dependence, then it is not clear how to incorporate these features into more accurate thermodynamic models.

D. Contrast of electronic features

It remains to gather further insight into the electronic processes which govern the different ordering tendencies in these cobalt-titanium and nickel-vanadium alloys. As already discussed, the densities of states [Figs. 1(a) and 1(b)] show (roughly) half-filled split-band states and hence, on band-filling grounds, an ordering mechanism is expected. For more detail, we compare Figs. 1(a) and 1(b) of the disordered alloys’ densities of states with the comparative plots of the $L1_2$ and $D0_{22}$ ordered alloys provided by Pei et al.$^2$ [their Figs. 4(a)–4(d)]. Disordered Co$_{25}$Ti$_{25}$ has more higher-energy states occupied around $\varepsilon_F$ than does the $L1_2$-ordered counterpart, and fewer such states than does the $D0_{22}$ one. This is consistent with strong $L1_2$ correlations from a band-filling origin that our calculations find. This feature is also present in Ni-V although less distinct.

The main difference between these two binary alloy systems comes from the behavior of charge transfer. In Co$_{25}$Ti$_{25}$, the large density of states at $\varepsilon_F$ of 24.2 states/atom Ry ensures that the effects from this are efficiently screened. This screening is predominantly carried out by states associated with the cobalt sites, i.e., $\Delta n(\varepsilon_F)$ is large, 18.8 states/atom Ry. All three terms in Eq. (6) are important in the interpretation of the results. In contrast, since both $\overline{n}(\varepsilon_F)$ and $\Delta n(\varepsilon_F)$ are smaller in Ni$_{17}$V$_{25}$ (17.4 and $-1.3$ states/atom Ry, respectively) the screening is less effective, so the compositional correlation function around $(1,\frac{1}{2},0)$ originates predominantly from incompletely screening of charge transfer. As the
temperature is increased, the discontinuity at the Fermi level is thermally broadened and, consequently, the intensity around \((1, \frac{1}{2}, 0)\) in \(\alpha(q)\) is diminished as the effective screening is improved. For \(Pd_{7/2}V_{2/2}\), the smaller effective change charge transfer and screening reduces the tendency toward \((1, \frac{1}{2}, 0)\)-type ordering even further. This smaller effective charge transfer results from the larger \(d\)-band width of \(Pd\). Normally, with a large-atom–small-atom alloy, the tails of the \(Pd\) charge density would “spill over” to the neighbor \(V\) atomic sphere causing large charge transfer to the \(V\) sites. This reduces the electronegativity effect which causes charge to be transferred from the early TM to the late TM and the net charge transfer is small.

The large width of the \(Pd\) \(d\) band, and the hybridization between \(Pd\)- and \(V\)-related states at low energies, has the effect of making the \(V\) states more prominent at \(e_F\). For this alloy, \(\overline{\rho}(e_F)\) and \(\Delta\rho(e_F)\) are 15 and \(-16.3\) states/atom \(Ry\), respectively.

Finally, in regard to the specific cutoff \(e/a = 8.65\) for \(D\) ordering behavior, there is no obvious explanation. However, in these split-band alloys, the percentage population of the \(t_{2g}\) states has an interesting characteristic. For the \(Ni\) and \(Pd\) alloys the \(e_g\) states are always greater than 85% populated. Given this, if more than 85% of the \(t_{2g}\) states of the late transition metal are occupied, then it appears that the alloy will form a low-temperature \(D\) phase. For \(Ni-V\) alloys with more than 70% nickel, this is found. For \(Pd_{7/2}V_{2/2}\) this percentage is 85%, just borderline. In the case of the Co alloy, both the \(t_{2g}\) and \(e_g\) populations are well below this critical value. While the occupations of the \(s\) and \(p\) states are relevant to the overall \(e/a\) ratio, they do not seem particularly correlated to the ordering trend. However, we stress that this particular feature of the \(t_{2g}\) population is only applicable for the split-band systems which result from alloying late transition metals with early ones.

In summary, we have uncovered a possible mechanism to explain the reasons for the ordering tendencies in \(Co_3\) and \(Ni_3V\), namely, why \(Co_3Ti\) has \(L_12\) while \(Ni_3V\) possesses a \(D\) structure at low temperature. This required a careful and consistent treatment of the doubling-counting contributions, as also found in the similar alloys of \(Ni-Cr\) presented in the companion paper. Moreover, we find that the theoretical estimates of the short-range order intensities for \(Ni_3V_{2/2}\) and \(Pd_{7/2}V_{2/2}\) are in fair agreement with those deduced from the high-temperature neutron data of Solal and co-workers. In addition, we have found a subtle temperature and concentration variation in our calculations for the nickel-vanadium system; we propose that these subtle variations be investigated by experiment. Finally, we have indicated the importance of changes in the electronic structure, and hence the interactions, when comparing quantities obtained from high-temperature measurements or calculations and low-temperature band-structure calculations.

V. SRO IN \(Ni_{50}Pt_{50}\): AN UPDATE

In a recent paper, we explored the short-range order in stoichiometric \(NiPt\) to understand the electronic origin of that system’s ordering tendency at high temperatures. The alloy \(NiPt\), with its \(d\) bands almost filled, was interesting because it stands as a glaring exception to traditional band-filling arguments from tight-binding theory: that a transition-metal alloy will cluster (phase separate) if the Fermi energy \(e_F\) lies near either band edge. In fact, the \(NiPt\) system strongly orders, with its phase diagram being similar to that of the noble-metal \(Cu-Au\) alloy system.

Our central result was that, despite a nearly filled \(d\) band, high-temperature (nonrelativistic) \(Ni_{50}Pt_{50}\) showed a (100)-order tendency which is commensurate with the low-temperature, \(L_10\)-ordered phase observed experimentally. Unlike previous tight-binding calculations, we included several electronic effects on an equal footing within the approximation of considering changes in electronic-structure only. As \(NiPt\) is an isoelectronic alloy, it was supposed that explicit electrostatic effects should be screened out and play no role in the ordering tendency. As such, static displacements and their effects on explicit charge transfer were also not considered. Nonetheless, the band-energy-only contributions can, as we found, reflect many aspects of Hume-Rothery’s empirical rules (i.e., difference in atomic sizes, \(e/a\), and electronegativity) for chemical and structural order in alloys, including (sometimes) competition between such factors. Complete details can be found in Ref. 28; in particular, for \(NiPt\), a size effect was described which was manifested in terms of the electronic structure, and was the basis for Hume-Rothery’s 15% (size-effect) rule.

Originally, as noted above, we did not consider directly the effects of relativity within the electronic-structure calculations, although it was determined that these effects could only alter the quantitative, not the qualitative, results. Unfortunately, the omission of these effects resulted in an apparent disagreement with calculated ground-state formation energies for \(L_10\) \(NiPt\). Thus, Lu, Wei, and Zunger have suggested that relativity is solely responsible for long-range, crystallographic order in \(NiPt\). Their reasoning is as follows. Nonrelativistic \(L_10\) has a formation energy that is unstable relative to phase separation, whereas relativistic \(L_10\) has a stable formation energy; hence, relativity causes chemical ordering. But this is neither the ordering mechanism nor the correct comparison. Experimentally, \(NiPt\) forms a good solid solution over the entire concentration field at high temperatures. So what causes long-range order when the disordered solid solution is cooled? Not relativistic effects, according to Wu, Wei, and Zunger’s results, since their approximation to the high-temperature state is also stable relativistically. Relativistic effects in the form of Darwin and mass-velocity terms are responsible for stabilizing both the \(L_10\) alloy and the solid solution. Our results and theirs are not at odds, as we have explained elsewhere. The methods are complementary and should be used as such.

In order to update the results for \(NiPt\) and to give a complete perspective of the theory as it is currently developed, we show the results for scalar-relativistic calculations for \(NiPt\) in which only the variations of the electronic-structure terms have been kept for comparison.
to our nonrelativistic results. Our results remain unchanged qualitatively. Next, the results are given for scalar-relativistic NiPt when all terms in the grand potential are considered, save the effects of static lattice displacements.

A. Scalar-relativistic \( S^{(2)} \) from band energy only

In Fig. 5, for Ni\(_{50}\)Pt\(_{50}\), we plot \( \alpha(q) \) at \( T = 1235 \) K (200 K above our \( T_{sp} \)) in the \( q_z = 0 \) plane of the extended zone. The cavity-field correction has not been included for comparison to the original work.\(^{28}\) Clearly \( S^{(2)}(q) \) peaks at the (100) Lifshitz special point, indicating instability to \( L1_0 \) ordering. This calculation is based on scalar-relativistic, SCF-KKR-CPA potentials\(^{44}\) for disordered Ni\(_{50}\)Pt\(_{50}\) at the experimentally observed lattice spacing. As described in Ref. 28, the ordering tendency as described by \( \alpha(q) \) arose from electronic states well below the Fermi energy, resulting from hybridization, indicating also that the ordering tendency is insensitive to the exact position of \( E_F \), and, thus, to changes in the \( e/a \) ratio. These bonding states, mainly corresponding in energy to the lower half of the Ni \( d \)-band complex, have \( t_{2g} \) symmetry with lobes pointing toward the nearest neighbors in the fcc structure, ensuring that the peak of \( \alpha(q) \) will occur at the \( X \) points. Details of the electronic mechanism may be found in Ref. 28.

By lattice Fourier transforming \( S^{(2)}(q) \), we obtain a real-space shell by shell representation, \( S^{(2)}_n \). These chemical interchange energies for the first four neighbor shells are \(-3.9, -0.8, -0.3, \) and \(1.2 \) mRy, respectively. Clearly, the nearest-neighbor \( S^{(2)}_{n=1} \) dominates, which implies a robust ordering, as was deduced from experiment by Dahmani \textit{et al.}\(^{45}\) Our calculated, man-field \( T_{sp} \) of 1035 K is in good agreement with the observed 918 K.\(^{45}\) This is to be compared with a \( T_{sp} \) of 1500 K in the nonrelativistic calculations.\(^{28}\) Thus, as suggested originally,\(^{28}\) relativistic effects are important for lowering \( T_{sp} \) but not for improving the qualitative picture (see below). By including the Onsager corrections in this band-energy-only approximation, the topology remains but \( T_{sp} \) is lowered to 700 K. Of course, the \( S^{(2)}_n \) parameters are the same as above, for it was the Onsager \( \lambda \) (calculated to be 5.8 mRy) which reduced \( T_{sp} \).

While (100)-type ordering fluctuations are found to be favorable, we find the \( (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) fluctuations to be nearly energetically. In other words, we find a smaller, subsidiary peak at \( (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) (or the \( L \) point). This peak arises from a mechanism related to states at the top of the Pt \( d \) band. (A detailed discussion of the \( L \)-point ordering tendency and its origin will appear elsewhere.) The difference between the \( S^{(2)} \) at \((1,0,0)\) and \( (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) is about 22\% at 1100 K. It would be worthwhile to determine experimentally if there is any substantial diffuse intensity scattering around the \( L \) point, as we have predicted.

B. Scalar-relativistic \( S^{(2)} \): Beyond band energy

Having obtained such good agreement with the experimental data for the type and robustness of the SRO and the transition temperature for NiPt alloys, one would suspect that including other contributions, namely electrostatic and displacement effects, would just be filling in details. However, the NiPt system actually seems to be somewhat more subtle than at first we suspected.

We note that the similarity of the electronegativity of Ni and Pt implies that each atom will have to be more or less neutral in the alloy, and hence charge-transfer effects should be small. However, because we have used the equal-sphere ASA in the calculation, we find roughly 0.15 electrons transferred to the Ni sites from the Pt sites, giving a \( \Delta Q \) of 0.3 electrons within the current framework. This charge comes from the tails of the Pt charge densities and must produce non-neutral sites because of the rigid-lattice and equal-sphere constraints. The result is a rather significant electrostatic contribution to the SRO, which, in the rigid-lattice formulation given here, remains incompletely screened.

When all terms in the grand potential are used in the calculation of the diffuse intensity, in particular the electrostatic terms [the last two terms of Eq. (6)], the peaks in \( \alpha(q) \) no longer occur at the \((1,0,0)\) points, i.e., \( X \) points. Due to an incomplete screening, the electrostatic terms enhance both the \((1,\frac{1}{2},0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) fluctuations, shifting the maximum in \( \alpha(q) \) to the \( L \) point. Recall that the \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) fluctuations were nearly energetically to the \((1,0,0)\), such that a small peak already existed in the band-energy-only case. These new terms also diminished the intensity at the \( X \) points enough so that peaks are no longer produced at the \( X \) points. Quantitatively, at 1000 K, the full \( S^{(2)} \) including Onsager corrections are \( 0.01136, 0.02300, \) and \( 0.02077 \) Ry for the \( X, L, \) and \( W \) points, respectively; whereas, for the band-energy-only case without Onsager corrections, these values were
0.02626, 0.02084, and 0.00765 Ry, respectively. This shows how the electrostatic terms tend to favor the larger-magnitude vectors within the Brillouin zone. Slightly more screening, probably due to static displacements, would effectively cancel the (rigid-lattice) electrostatic contributions, leaving the atomic short-range order to be solely determined by the electronic-structure changes (band-energy variations). As stated before, this would be in keeping with our intuition for isoelectronic alloys. Note that the local displacements would not only directly influence the charge on each site, and thereby the electrostatics, but would also have a large effect on the screening of those charges through increased disorder broadening of the local electronic structure.

As physical arguments suggest and tight-binding methodology requires, isoelectronic alloys should have effectively charge-neutral atoms. So our results, which ignore the electrostatic contributions, and are in very good agreement with experimental transition temperatures, should contain the correct physics. To describe properly this charge neutrality in isoelectronic systems (i.e., electronic screening) requires a subtle but rigorous description within a first-principles approach. So again, it appears that static lattice displacements do play an important role in determining the ASRO.

That the coupling of the chemical degrees of freedom and the lattice is important should come as no surprise. Experiments, such as XAFS, show rather large displacement effects in 3d-5d alloys. It has been suggested that this coupling is responsible for the CuAuII phase in the Cu-Au phase diagram. Simulations of the Cu-Au phase diagram using the embedded atom method find that displacements affect the widths in concentration of the low-temperature phase fields.

In summary, for NiPt, we have found that the SCF-KKR-CPA theoretical framework predicts an ordering tendency in NiPt alloys which is critically related to the balance of diagonal and off-diagonal disorder, providing an electronic origin for the ordering in big-atom–little-atom transition-metal systems. The effects of relativity are not important for the purpose of understanding the origins of ordering in this system, although they are necessary for obtaining a more accurate prediction of the transition temperature. Significantly, however, we suggest that static displacements appear to be important in reducing the effective charge transfer and improving screening. In other words, as argued above, only the band-energy contributions dictate the type of SRO for NiPt, with the displacement and electrostatic terms canceling one another. Although this is not true in general, physical arguments, as given originally by Treglia and Ducastelle and backed up by our results, suggest that the band-energy effects hold the key to the compositional ordering and appear to be valid for isoelectronic alloys.

VI. $D_0_{19}$ ORDERING IN Al$_{75}$Ti$_{25}$: PRESENCE OF COMPETING INTERACTIONS?

In the case study of the Cu$_{75}$Pd$_{25}$ alloy described in the companion paper, we confirmed the findings of Gyorffy and co-workers that the long-ranged, incommensurate order observed in this system can be understood as originating from a mechanism associated with well-defined sheets of the Fermi surface of the disordered alloy. Titanium-aluminum, in the vicinity of the composition range of 25% Ti, also possesses a fascinating collection of long-period phases which were studied by Loiseau et al.

Consequently, we pose some questions of our theoretical formalism concerning the nature of the ordering mechanisms at work in this system. Is there a Cu-Pd-like Fermi-surface mechanism at play in this alloy? Or, since it has been conventional to describe the long-period phases in terms of an axial, next-nearest-neighbor, Ising (ANNNI) model, do the first-principles electronic-structure calculations indicate instead effective, competing short-ranged interactions?

For the stoichiometry of 25% Ti, the alloy orders into $D_{022}$ phase on solidifying. Hence our calculated compositional correlation function of a compositionally disordered alloy should show maxima at the special points $(0,0,1)$ and $(0,1,1)$, i.e., the $X$ and $W$ points. Moreover, the ordering temperature deduced from these calculations should be greater than the melting temperature. Our first step was to carry out SCF-KKR-CPA calculations of the high-temperature, compositionally disordered, fcc alloy, which in this case does not exist in nature. We assumed a lattice spacing of 7.5 a.u., extracted from experimental measurements on the ordered phase, which, together with the atomic numbers of constituents, were the only parameters input to the calculation.

In Fig. 6 we depict the averaged and partially averaged density of states for this alloy weighted by the appropriate concentration factors. Essentially, we see broad $s$-$p$ states associated with both types of sites and "virtually bound" $d$ states associated with titanium around the Fermi energy. According to our definition, there is only a small $\Delta Q$ transfer of 0.06 electrons from titanium to aluminum in this alloy. The density of states

![Graph](image-url)
at the Fermi energy of 9 states/Ry is quite low and so we expect charge-rearrangement effects to be small and the effective interchannel energy to be dominated by $S^{\text{band}}(q)$, the band-filling contribution. We investigated the electronic structure around the Fermi energy in order to assess the likelihood of a Fermi-surface component producing a long-ranged, complicated interaction. Just as Gyorffy et al. discovered, the Fermi-energy electronic structure is strongly smeared by the compositional disorder and no Fermi-surface mechanism is at play in this alloy.

This is indeed the case described by our full calculations, which are shown in Fig. 7. Strong ordering correlations for an $L1_2$ (Cu$_3$Au) phase are found with an estimated transition temperature of 3300 K, well in excess of the alloy's melting temperature. As previously done, we made a fit of $S^{(2)}(q)$ to real-space parameters. At $T=3500$ K, $S^{(2)}_{13} = -13.2, 6.9, -3.1, 2.3,$ and $1.2$ mRy, respectively, with the constant term $S^{(2)}_0 = -29.2$ mRy. Additions from more distant shells are all less than 1 mRy in magnitude. There is no evidence of competing ANNNI-like parameters, nor correlations which might lead to the establishment of a $D0_{22}$-ordered phase at this concentration, i.e., there are no maxima at the $(1,1,0)$ special points.

Gyorffy et al. reported the uncovering of a similar situation from their calculations of $\alpha(q)$ in which only the band-filling part of $S^{(2)}(q)$ was considered. These same authors also described some total-energy calculations which are consistent with these results. LMTO calculations of the total energy of $D0_{22}$ and $L1_2$-ordered Al$_3$Ti were carried out on the same underlying fcc lattice and it was found that the latter $L1_2$ structure was the more stable. On the incorporation of a tetragonal distortion to the fcc lattice using the experimental $c/a$ ratio, this situation was reversed and the $D0_{22}$ structure was preferred. This was also found by Carlsson, who also investigated ternary additions.

Gyorffy et al. suggested, from the basis of this work, that an important coupling between lattice distortions and compositional fluctuations may be present in this system. This, they propose, ultimately leads to effective competing interactions which are responsible for the rich variety of phases in Ti-Al alloys. Since our single major approximation has been to constrain the underlying lattice to be rigid and hence neglect any lattice displacement and strain effects, we strongly favor this suggestion as the dominant source of the discrepancy. If this indeed is the case, the effect of static displacements in the Al-Ti system is different than in the Ni-Pt system, where we have supposed that atoms move so as to rearrange charges in order to screen out more thoroughly the electrostatic contributions to the ASRO. We are planning future developments in which such effects are treated as carefully as those which we have incorporated to date.

VII. CONCLUSIONS

In this paper, we have explored our theory of compositional correlations in metallic alloys, which we have detailed in a companion paper, by presenting calculations for five different alloy systems. The aspect of the work which we have emphasized is its grounding in a first-principles description of the underlying electronic structure. This is in common with much complementary work in this area. Within this mean-field approach, the description both of the compositional fluctuations and of the itinerant electrons which sustain them are mutually consistent. By incorporating the cavity fields proposed by Onsager, the diffuse scattering intensity is conserved over the Brillouin zone, atypical of mean-field theories. The Onsager description was found to be important when dealing with longer-ranged, electrostatic interactions. For a rigid lattice, all electronic effects have been included within this Onsager approximation. Thus both band-filling effects and charge-rearrangement effects (arising from the double-counting terms) have been dealt with on a par. It is the treatment of the latter effect and an evaluation of its importance which is our main contribution.

We have attempted to originate Hume-Rothery's empirical rules of $e/a$ (band filling), electronegativity, and size from a quantum-mechanical or completely electronic basis.

The case study of Ni$_{75}$V$_{25}$, Pd$_{75}$V$_{25}$, and Co$_{75}$Ti$_{25}$ has uncovered (only partly) the electronic mechanisms which cause the first two alloys to form $D0_{22}$-ordered phases while the third forms an $L1_2$-ordered alloy in the solid phase. For the Ni and Pd alloys, we find very good agreement between the measured diffuse scattering intensities and our calculated ASRO. Also, for the Ni-V system, subtle changes in ordering due to concentration and temperature effects were found; these changes arose from a combination of band-filling and screening effects. Some of our results are supported by experiment and by other
electronic-structure calculations. We emphasize that these good descriptions are only possible because of the careful treatment of the double-counting contributions to the grand potential, which heretofore have been ignored in many theories of ASRO. For all the alloys discussed we have also shown how the results are affected when the double-counting contributions are neglected. We also emphasized the importance of the changes in the electronic structure upon a symmetry transformation, which explains the previous discrepancies related to comparisons of chemical interactions from high-temperature measurements and calculations (such as ours) and $T=0$ K band-structure calculations. Our theoretical results tie in well with Sinha's empirical rule\(^{29}\) that $A_{75}B_{25}$ fcc-based alloys form $D_{022}$ phases if the average number of valence electrons per atom is greater than 8.65, while those with fewer have the likelihood of establishing $L_1^2$ structures. While no significance to $e/a$ of 8.65 was found, the occupancy of the $f_{2g}$ and $e_g$ states of the late transition metal in these split-band systems appeared to follow a trend. A key feature, however, was the density of states at the Fermi level associated with the late transition metal. Roughly speaking, for systems with $e/a$ less than 8.65 (or $d$-band occupation of less than 85%) like $\text{Co}_7\text{Ti}_{25}$, a large $n(e_F)$ provided a large screening and the tendency for $L_1^2$-type fluctuations; whereas for a greater $e/a$ there were fewer states at $e_F$ associated with the late transition metal, and hence less screening, and we found $D_{022}$-type fluctuations.

At several points, we have emphasized that the major approximation of this work is that the underlying Bravais lattice is fixed and not allowed to distort in response to concentration modulations. That is, chemically induced strain fluctuations are not included. This shortcoming is likely to be most important for alloys with constituents of differing atomic sizes, for example, alloys of transition metals from differing rows in the periodic table, or alloys of a simple metal with a transition metal. Consequently, we assessed the severity of the neglect of these effects by our calculations for the compositional correlations of two such metal alloys, $\text{Ni}_{50}\text{Pt}_{50}$ and $\text{Al}_{75}\text{Ti}_{25}$. Our scenario for the former, isoelectronic alloy is that the lattice distorts so as to minimize the charge rearrangement (to maximize charge neutrality) and that the net result is that the compositional correlations are effectively set up by band-filling effects as assumed in previous calculations.\(^{28}\)

As a partial confirmation of this, a prediction was made for additional small peaks in the diffuse intensity at the $L$ points for NiPt. Our final case study on $\text{Al}_{75}\text{Ti}_{25}$ did not indicate either the source of $D_{022}$ correlations nor the reason for the devil's staircase of phases found in this system. It seems that the panoply of a theory in which both compositional and lattice-strain fluctuations are treated on an equal footing is needed. The bones of such a theory have been set out by Gyorffy $et\ al$.\(^{31}\) and we are planning for its development and implementation, with $\text{Al}_{75}\text{Ti}_{25}$ being an ideal first candidate.

**ACKNOWLEDGMENTS**

This work was partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, through a New Initiative under Contract No. DE-AC04-94AL85000, by SERC in the U.K., by Cray Research, Inc., and by NATO. In addition, we acknowledge grants from the Ohio Supercomputer Center and the Sandia Computer Center. D.D.J. thanks Mark Asta for useful conversations and Alphonse Finel for correspondence. Also, we thank Chris Wolverton and Alex Zunger for pointing out an error in the original draft.


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